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Published in:
The Journal of Chemical Physics

DOI:
10.1063/1.433137

Unified rotational dynamics of molecular crystals with orientational phase transition*

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(Received 5 April 1976)

A unified theory for the rotational dynamics of molecular crystals with orientational phase transitions is given. As basic secular variables one takes symmetry adapted functions, which describe the molecular orientations, and the angular momenta of the molecules. Using Mori's projection operator technique, one obtains a coupled set of two dynamic matrix equations for the corresponding relaxation functions. The coupling is proportional to the order parameter and accounts for the reactive coefficients. The corresponding collective excitations are librons. The damping of librons is described by two transport coefficients that account for orientational relaxation and angular momentum relaxation, respectively. By approaching the phase transition, both matrix equations decouple, the orientational relaxation describes the critical dynamics. In the disordered phase, this equation describes collective hindered rotations. In the same framework one describes phases of partial order as CD_4 II. Comparison is made with neutron scattering experiments.

I. INTRODUCTION

The study of librons in molecular crystals usually starts from the assumption that the molecules perform small rotational oscillations around well defined equilibrium positions. The dynamic variables are then the angular displacements φ (expressed, for example, in terms of Euler angles) and the momenta (conjugate to the Euler angles).[1-3] One also can take the atomic displacements and their conjugate momenta as dynamic variables[4]; thereby one makes no distinction between translational and rotational degrees of freedom. In any case, it is generally not sufficient to restrict oneself to a harmonic theory if one wants to describe the rotational dynamics of molecular crystals. Indeed, the multipolar forces that are responsible for the molecular orientations are generally weak; therefore the rotational amplitudes are very large.[5,6] An expansion of the potential energy in terms of rotational displacements has to take into account anharmonic terms to any order. In this respect the problem is similar to the dynamics of quantum crystals.[7] Therefore one takes over the methods such as time dependent Hartree[8] and self-consistent phonon theories[4] to treat the rotational dynamics.

However, these approaches remain unsatisfactory in many ways. The temperature variation of the libron frequencies, particularly if one approaches the phase transition, is not well explained.[4] Also, the damping of librons remains a difficult problem.[9] The same observation can be made about the treatment of anharmonic terms arising from the kinetic energy. It is only for the harmonic case (small angular deviations) that the kinetic energy is a sum of squares of the conjugate momenta of the Euler angles.

In a previous paper[10] by Kroll and one of the present authors, an attempt was made to describe the dynamics of molecular crystals, in particular librational excitations and their damping. Much attention was given to the problems and difficulties just mentioned, and progress in their solution could be achieved. In a further publication by the same authors,[11] the dynamics of molecular crystals at orientational phase transitions was given. In particular, recent neutron scattering experiments[12] on critical dynamics in CD_4II were explained on the basis of the theory.

Despite the results obtained in Refs. 10 and 11, some questions remain. In our opinion the principal one is the following: How can one describe by a single theory (i.e., in an unified way) the dynamics of molecular crystals in the ordered phase as well as in the disordered phase and near the phase transition? In Refs. 10 and 11, different sets of dynamic variables were chosen for the description of the ordered and the disordered phase. In the first case the angular deviations and their conjugate momenta were chosen as secular variables, while for the disordered phase and the critical dynamics, symmetry adapted functions were needed. It is then obvious that it was not possible to describe the transition from the fully ordered phase to the disordered phase in a continuous way.

In the last few years a method has been developed[13] for the analysis of orientationally disordered structures. It is based on the expansion of physical quantities in a complete set of symmetry adapted functions. The method is also suited for the description of ordered phases with molecules performing large librational motions. It has been applied to study the statics[14,15] and the dynamics of critical phenomena and of the disordered molecules[10,11] in CD_4II. Here we will present a new formulation of libron dynamics based on the concept of symmetry adapted functions.[16] The plan of the paper is as follows.

In Sec. II we recall some basic relations of dynamic response theory. We will use the Mori–Zwanzig[17] projection operator technique to derive the response functions. Next (Sec. III) we present the Hamiltonian for orientational interactions. The kinetic energy is written as a quadratic function of the angular momenta, while the multipolar interaction potential is formulated as a bilinear expression of the symmetry adapted functions. In addition to the symmetry adapted functions, we take the angular momenta of the molecules as dynamical variables. For these variables, the dynamic

response functions are derived in Sec. IV. We obtain a coupled set of two matrix equations, the first one essentially describing the relaxation of orientational correlations and the second one the relaxation of angular momentum. The coupling between the two equations is provided by the restoring forces. A discussion of these basic equations is given in Sec. V. Depending on temperature, the basic equations describe the dynamics of (a) fully ordered phases, (b) fully disordered phases, and (c) phases of partial order as well as the transition between these different cases. Finally (Sec. VI), we consider the dynamic neutron scattering law and discuss the resonances as a function of temperature.

II. BASIC RELATIONS

In this section we recall without proof some known concepts of dynamic response theory. For a detailed derivation, the reader is referred to the quoted literature. Here and in the following, we use units where $\hbar=1$, $k_B=1$.

The thermal average of an operator A is defined by

$$\langle A\rangle = \mathrm{Tr}[\exp(-H/T)A]\{\mathrm{Tr}[\exp(-H/T)]\}^{-1} . \tag{2.1}$$

As usual, H denotes the Hamiltonian of the system and T stands for the temperature. The time evolution of the operator A is given by

$$A(t) = e^{i\mathfrak{L}t}A , \tag{2.2a}$$

where $\mathfrak{L}$ is the Liouville operator defined by

$$\mathfrak{L}A = [H,A] . \tag{2.2b}$$

In linear response theory the response function of two operators A and B is related to the Laplace transform of the retarded Green's function[18,19]:

$$\chi_{AB}(z) = -\langle\langle A^\dagger; B\rangle\rangle_z = i\int_0^\infty dt\, e^{izt}\langle[A^\dagger(t), B(0)]\rangle , \tag{2.3}$$

with $\mathrm{Im}z>0$. The relation between the Laplace transform of Kubo's relaxation function[20]

$$\Phi_{AB}(t) = \int_t^\infty dt'\, e^{-\epsilon t'}\langle[A^\dagger(t'), B(0)]\rangle \tag{2.4a}$$

and the response function is given by[19]

$$\Phi_{AB}(z) = \int_0^\infty dt\, e^{izt}\,\Phi_{AB}(t) = \frac{1}{z}[\chi_{AB}(0) - \chi_{AB}(z)] . \tag{2.4b}$$

The dynamic form factor measured by neutron or light scattering experiments is obtained from

$$S_{AB}(\omega) = [1-\exp(-\omega/T)]^{-1}\,\mathrm{Im}\chi_{AB}(\omega), \qquad \omega\in\mathfrak{R} . \tag{2.5}$$

Starting from the assumption that for the time scale of interest the dynamics of the system is governed by the behavior of a set of secular variables $\{A_\mu\}$, we use the Zwanzig–Mori projection operator technique to calculate the dynamics of the secular variables.

Following the general theory,[17,21] we define a scalar product of two operators A_α and A_β by

$$(A_\alpha, A_\beta) = \chi_{\alpha\beta}(0) . \tag{2.6}$$

The relaxation function Φ obeys the matrix equation[21]

$$[z\delta_{\mu\lambda} - \Omega_{\mu\lambda} + \Sigma_{\mu\lambda}(z)]\Phi_{\lambda\nu}(z) = \chi_{\mu\nu}(0) . \tag{2.7}$$

The matrix of restoring forces is given by

$$\Omega_{\mu\lambda} = (A_\mu, \mathfrak{L}A_\nu)\chi^{-1}_{\nu\lambda}(0) , \tag{2.8}$$

while the dissipation matrix is obtained from

$$\Sigma_{\mu\lambda} = -(Q\mathfrak{L}A_\mu, (z - Q\mathfrak{L}Q)^{-1}Q\mathfrak{L}A_\nu)\chi^{-1}_{\nu\lambda}(0) . \tag{2.9}$$

Here Q is the projector onto the space of nonsecular variables

$$Q = 1-P, \qquad PA = \sum_{\nu,\mu} A_\nu \chi^{-1}_{\nu\mu}(0)(A_\mu, A) , \tag{2.10}$$

while P projects onto the space of secular variables. From the equation of motion of the retarded Green's function[18]

$$z\langle\langle A^\dagger; B\rangle\rangle_z = \langle[A^\dagger, B]\rangle + \langle\langle[A^\dagger, H]; B\rangle\rangle_z \tag{2.11}$$

and the definition of the Liouville operator we find

$$(A, \mathfrak{L}B) = \langle[A^\dagger, B]\rangle . \tag{2.12}$$

Expression (2.8) shows that the restoring forces are essentially given by the projections of the currents $\mathfrak{L}A$ on the secular variables themselves, while the dissipative effects [see Eq. (2.9)] arise from correlations of nonsecular parts of the currents.

In Sec. IV we will need the following symmetry relations:

$$(A,B) = (A^\dagger, B^\dagger)^* = (B^\dagger, A^\dagger) = \overline{(\bar{A}, \bar{B})}^* , \tag{2.13}$$

where $\bar{A}$ denotes the time reversed operator.

III. THE MODEL

A. The Hamiltonian

We start from a lattice of known structure and assume that the centers of mass of the molecules are fixed on rigid lattice points. This means that in the present context we will neglect translational degrees of freedom (phonons). This is of course an approximation, but in the present paper we will restrict ourselves to a treatment of rotational degrees of freedom only. As a further but probably less significant approximation we will neglect the internal excitations of the molecules. Consequently we consider the molecules as rigid bodies with known principal moments of inertia I_1, I_2, I_3.

Taking the moving (molecular) system of coordinates along the principal axes (ξ,η,ζ) of the molecules, we have for its kinetic energy

$$K_1 = \frac{1}{2}\left(\frac{L_\xi^2}{I_\xi} + \frac{L_\eta^2}{I_\eta} + \frac{L_\zeta^2}{I_\zeta}\right). \tag{3.1}$$

Restricting ourselves to a lattice of identical molecules with spherical top symmetry (for instance, tetrahedral molecules as for CH_4), we have $I_\xi = I_\eta = I_\zeta = I$. Then the total kinetic energy reads

$$K = \frac{1}{2I}\sum_\rho (L^2_{\xi,\rho} + L^2_{\eta,\rho} + L^2_{\zeta,\rho}) . \tag{3.2}$$

The sum runs over all lattice points. Here $\rho\equiv(\mathbf{n}, a)$, where $\mathbf{n}$ is the unit cell index, and a denotes the molecules within a unit cell. The orientation of a molecule ρ with respect to the laboratory (fixed) frame can be specified by the three Euler angles $\varphi_\rho\equiv(\alpha_\rho,\beta_\rho,\gamma_\rho)$.

Assuming a two body multipolar interaction, the orientational potential between two bodies ρ and ρ' can be written as[22,23]

$$V_{\rho\rho'} = \sum_{l,l'}\sum_{i,i'}\sum_{j,j'} A_{\rho\rho'}\begin{pmatrix} ll' \\ ii' \\ jj' \end{pmatrix} D^{l}_{ij}(\varphi_\rho) D^{l'}_{i'j'}(\varphi_{\rho'}) \ . \qquad (3.3)$$

Here the D^l_{ij} are the Wigner D functions and $A_{\rho\rho'}$ is a geometrical coupling tensor.

If the molecules are orientationally not well localized—in other words, if the amplitudes of orientational oscillations are rather large in the ordered phase or if the molecules carry out a motion of rotational diffusion—it is more convenient to take a set of symmetry adapted functions[13,24] $\{U^l_{ij}\}$ instead of the Wigner D functions. The U functions are related to the Wigner D functions by a unitary transformation $U = SDS^{-1}$ and constitute a representation of the rotation group. Expressing the two body interaction in terms of U functions, one finds for the orientational potential of the crystal[24]

$$V = \sum_{\rho\rho'} V_{\rho\rho'} = \sum C_{\rho\rho'}\begin{pmatrix} ll' \\ ii' \\ jj' \end{pmatrix} U^{l}_{ij}(\varphi_\rho) U^{l'}_{i'j'}(\varphi_{\rho'}) \ , \qquad (3.4)$$

where in the last member of this equation the summation runs over all repeated indices. Then the Hamiltonian we will use in the following is given by

$$H = K + V \ , \qquad (3.5)$$

where K and V are defined by Eqs. (3.2) and (3.4), respectively.

As an example we will apply our theory to CD_4, where excellent neutron scattering experiments[6,12,14,25] have been done. The lattice has a fcc structure. In the ordered phase II,[6,14] two out of eight molecules have no definite orientation while the remaining six molecules of the unit cell have a antiferrorotational order. The relevant multipolar interaction[24] is of octopole–octopole type, and the set of symmetry adapted U functions is given by the cubic rotator functions of order $l = 3$. As a consequence of the high symmetry of the molecule it is sufficient to take the set $\{U^3_{1i}\}$, $i = 1, \ldots, 7$.[24]

B. The secular variables

At the moment, it is well known[11] that one has to take the full set $\{U^3_{1i}\}$, $i = 1, \ldots, 7$ in order to describe the critical dynamics of CD_4II. Also, in order to describe the disordered (central) molecules in CD_4II, one had to use the full set. On the other hand, the dynamics of the ordered molecules in CD_4II was formulated in terms of Euler angles and their conjugate momenta $\pi \equiv (\pi_\alpha, \pi_\beta, \pi_\gamma)$ as secular variables.[10] As already mentioned in the Introduction, this choice is not optimal, as can be seen explicitly from the complicated form of the kinetic energy and of the commutation rules of the U functions with the momentum operators π.

In the present approach, we will take instead of the momenta π the spherical components L_0, L_+, and L_- of the angular momenta. These are defined by

$$L_0 \equiv L_\zeta \ , \qquad L_\pm \equiv \pm (L_\xi \mp i L_\eta)/\sqrt{2} \ , \qquad (3.6)$$

and their action on the Wigner D functions is very simple[26]:

$$L_p D^l_{mk} = \sum_{k'} a^{pl}_{kk'} D^l_{mk'} \ , \qquad p = 0, \pm \ , \qquad (3.7)$$

with

$$a^{0l}_{kk'} = k\delta_{k,k'} \ , \quad a^{\pm l}_{kk'} = \pm\sqrt{(l \pm k)(l \mp k + 1)}/\sqrt{2}\,\delta_{k\mp 1,k'} \ . \qquad (3.8)$$

Using this fact as well as the unitary transformation S, we find for the action of these operators on the U functions

$$L_p U^{(l)}_{ij} = i \sum_k b^{pl}_{jk} U^{(l)}_{ik} \ . \qquad (3.9)$$

The coefficients b^{pl}_{jk} are real. This is explicitly shown in Appendix A.

For convenience we define the Fourier-transformed operators

$$U^a_\nu(\varphi_\rho) = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{X}(\rho)} U^a_\nu(\mathbf{q}) \ , \qquad (3.10)$$

$$L^a_{p,\rho} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{X}(\rho)} L^a_p(\mathbf{q}) \ , \qquad (3.11)$$

where N is the number of unit cells. Here ρ stands again for $(\mathbf{n}, a)$; a is the sublattice index; and ν stands collectively for i, j, and l.

We will not expand the U functions in terms of Euler angles but consider instead the dynamics of the complete U functions. Thereby we automatically take into account the full anharmonicity of the problem.

After these remarks, the obvious set of secular variables is now

$$\{A^\alpha\} \equiv \{L^a_p(\mathbf{q}), U^a_\nu(\mathbf{q})\} \ , \qquad (3.12)$$

where a runs over all sublattices.

Finally we remark that it is easily possible to add the orthogonalized local energies to the set of secular variables. But as has been said previously, this is not of great physical interest and hence we will not do it here.[10]

IV. DYNAMIC RESPONSE FUNCTIONS

Having given the necessary elements of general dynamic response theory in Sec. II and having specified the model as well as the relevant secular variables in Sec. III, we are ready to derive the correlation functions that describe the rotational dynamics of molecular crystals.

Taking the set (3.12), i.e., $\{L^a_p(\mathbf{q}), U^a_\nu(\mathbf{q})\}$ as dynamic variables, we obtain for the static susceptibility matrix

$$\tilde{\chi}(\mathbf{q}, z = 0) = \begin{pmatrix} \tilde{D}^{-1} & \tilde{0} \\ \tilde{0}^\tau & \tilde{B}^{-1} \end{pmatrix} \ , \qquad (4.1)$$

where we have defined $\tilde{D}^{-1} = (U^a_\nu(\mathbf{q}), U^{a'}_{\nu'}(\mathbf{q}))$, $\tilde{B}^{-1} = (L^a_p(\mathbf{q}), L^{a'}_{p'}(\mathbf{q}))$, and $\tilde{0} = (U^a_\nu(\mathbf{q}), L^{a'}_{p'}(\mathbf{q}))$. The matrix $\tilde{0}$ is the zero matrix as follows from time reversal invariance. Generally we will use the index τ to designate the transposed matrix.

Making use of Eqs. (2.12) and (2.9) we introduce a matrix $\tilde{C}$ defined by

$$i\tilde{C}^{\tau}(\mathbf{q}) = i(U_{ij}^{la}, \mathcal{L}L_{\rho}^{a'}) = i\langle [U_{ij}^{la}, L_{\rho}^{a'}] \rangle$$

$$= \delta_{aa'} \sum b_{jk}^{\rho l} \langle U_{ik}^{la}(\mathbf{q}) \rangle \ . \qquad (4.2)$$

In a similar way, one finds

$$(U_{ij}^{la}, \mathcal{L}U_{jk}^{l'a'}) = 0 \ , \qquad (L_{\rho}^{a}, \mathcal{L}L_{\rho'}^{a'}) = 0 \ . \qquad (4.3)$$

With Eqs. (4.2) and (4.3), the restoring force matrix $\tilde{\Omega}$, defined by Eq. (2.8), is found to be

$$\tilde{\Omega}(\mathbf{q}) = \begin{pmatrix} \tilde{0} & -i\tilde{C}\tilde{B} \\ i\tilde{C}^{\tau}\tilde{D} & \tilde{0} \end{pmatrix} . \qquad (4.4)$$

The result (4.2) allows us to make some comments about the matrix C. We know that $U_{ik}^{la}(\mathbf{q})$ taken at specific points $\mathbf{q} = \mathbf{q}_0$ in the reciprocal lattice constitutes the order parameter variable, similar to the magnetization or the staggered magnetization in the ferro- and antiferromagnet, respectively.[27] Consequently, in the ordered phase one has $\langle U_{ik}^{la}(\mathbf{q}_0) \rangle \neq 0$ for certain values of the indices i, k, and a. The lowest multipole (lowest l) function with this property is the order parameter $\langle \sigma \rangle$ of our problem. For the disordered phase, this quantity vanishes on all lattice points for $T > T_c$, while for phases of partial order, $\langle \sigma \rangle \neq 0$ for $T < T_c$ on ordered sublattices and $\langle \sigma \rangle = 0$ for $T < T_c$ on disordered sublattices as, for instance, the "central molecule" in phase II of CD_4.[6,24] One realizes now that the present description is adequate to treat in a unified way phases of partial order.

We next consider the memory matrix Σ, defined by Eq. (2.9). Under the assumption that the time behavior of all nonsecular modes is much faster than the one of the secular modes, we can take $\Sigma(z)$ at $z = i0$. Remembering that $\Sigma_{AB}(i0)$ vanishes if $\mathcal{L}A$ and $\mathcal{L}B$ have opposite signature under time reversal, we find

$$\Sigma(i0, q) = \begin{pmatrix} i\tilde{\Lambda}_{UU} & \tilde{0} \\ \tilde{0}^{\tau} & i\tilde{\Lambda}_{LL} \end{pmatrix} \begin{pmatrix} \tilde{D} & \tilde{0} \\ \tilde{0}^{\tau} & \tilde{B} \end{pmatrix} = \begin{pmatrix} i\tilde{\Gamma}_{UU} & \tilde{0} \\ \tilde{0}^{\tau} & i\tilde{\Gamma}_{LL} \end{pmatrix} , \qquad (4.5)$$

where $\tilde{\Gamma}_{UU} = \tilde{\Lambda}_{UU}\tilde{D}$ and $\tilde{\Gamma}_{LL} = \tilde{\Lambda}_{LL}\tilde{B}$. Here we have defined [compare Eq. (2.9)]

$$i\Lambda_{AB} = -\lim_{z \to i0} (Q\mathcal{L}A, (z - Q\mathcal{L}Q)^{-1} Q\mathcal{L}B) \ . \qquad (4.6)$$

Using the time reversal properties of U and L as well as expression (4.1) for $\tilde{\chi}(0)$, we find from Eq. (2.10) that the projection of the currents $\mathcal{L}U$ and $\mathcal{L}L$ on the secular variables are given by

$$P\mathcal{L}U = L\tilde{\chi}_{LL}^{-1}(L, \mathcal{L}U) \ , \qquad (4.7a)$$

$$P\mathcal{L}L = U\tilde{\chi}_{UU}^{-1}(U, \mathcal{L}L) \ . \qquad (4.7b)$$

Here we have not written explicitly the indices of U and L. As $(L, \mathcal{L}U)$ and $(U, \mathcal{L}L)$ are only different from zero in the ordered phase, these projections are zero near T_c and in the disordered phase. Then $Q = 1$. As is well known,[19] an expression of type (4.6) can be rewritten as an anticommutator of the nonconserved parts of the currents (Kubo-type formula). The explicit evaluation of these transport coefficients is a very difficult problem in itself. For the case of a system of anharmonic phonons, it has been shown[21] that the evaluation of an expression of type (4.6) leads in first nontrivial approximation to integrals that are equivalent to those derived from Kohler's variational principle.[28] In the present treatment, we will not give an explicit calculation of this type, but only discuss the physical significance of the transport coefficients. We will estimate the numerical value of $\tilde{\Lambda}_{UU}\tilde{D}$ from experiment (Sec. VI).

With the use of Eqs. (4.1), (4.4), and (4.5), we rewrite Eq. (2.7) for $\tilde{\Phi}$ in block-matrix form for $z = \omega + i0$:

$$\begin{pmatrix} \omega\tilde{1} + i\tilde{\Gamma}_{UU} & i\tilde{C}B \\ -i\tilde{C}^{\tau}\tilde{D} & \omega\tilde{1} + i\tilde{\Gamma}_{LL} \end{pmatrix} \begin{pmatrix} \tilde{\Phi}_{UU} & \tilde{\Phi}_{UL} \\ \tilde{\Phi}_{LU} & \tilde{\Phi}_{LL} \end{pmatrix} = \begin{pmatrix} \tilde{D}^{-1} & \tilde{0} \\ \tilde{0}^{\tau} & \tilde{B}^{-1} \end{pmatrix} \qquad (4.8)$$

Here, of course, $\tilde{C}$, $\tilde{D}$, $\tilde{B}$, $\tilde{\Gamma}$, and $\tilde{\Phi}$ depend on $\mathbf{q}$, and $\tilde{\Phi}$ is a function of ω. From Eq. (4.8), we deduce the system of coupled matrix equations for $\tilde{\Phi}_{UU}$ and $\tilde{\Phi}_{LU}$:

$$(\omega\tilde{1} + i\tilde{\Gamma}_{UU})\tilde{\Phi}_{UU}(\omega) + i\tilde{C}^{\tau}\tilde{B}\tilde{\Phi}_{LU}(\omega) = \tilde{D}^{-1} \ , \qquad (4.9a)$$

$$-i\tilde{C}\tilde{D}\tilde{\Phi}_{UU}(\omega) + (\omega\tilde{1} + i\tilde{\Gamma}_{LL})\tilde{\Phi}_{LU}(\omega) = \tilde{0} \ . \qquad (4.9b)$$

From these equations we explicitly see that the transport coefficient $\tilde{\Gamma}_{UU}$ describes the decay of orientation correlations while $\tilde{\Gamma}_{LL}$ describes the decay of angular momentum correlations. The equations of $\tilde{\Phi}_{LU}$ and $\tilde{\Phi}_{UU}$ are coupled by the restoring force terms $C \propto \langle \sigma \rangle$. In the disordered phase and for disordered sublattices, no coupling exists.

At this time it is appropriate to make the connection with the dynamics in other systems. Equations (4.9a) and (4.9b) are formally very similar to the hydrodynamic equations of an n-component phonon system[29] or to those in magnetic systems.[27] We should mention, however, that in the present case L and U are not conserved quantities, as can be seen from the multipolar Hamiltonian. Consequently, the restoring forces and the "currents" are not proportional to q.

In ordinary phonon systems,[21] it follows from the presence of the operator Q in Eq. (4.6) and from the fact that $\dot{\mathbf{x}} = \mathbf{p}$, where x is the translation and p the conjugate momentum, that the transport coefficient Γ_{xx} does not exist. In libron systems $\Gamma_{\varphi\varphi}$ is different from zero only if one takes into account the anharmonicities of the kinetic energy.[10] Here Γ_{UU} leads to $\Gamma_{\varphi\varphi}$ if one expands $U_{(\varphi)}$ in powers of φ and takes the linear terms only.

We close this section with some observations on the dimensionality of the matrices considered here. For a given l and for a given sublattice a, U_{ij}^{l} generally has $(2l+1) \times (2l+1)$ components. If there are s molecules per unit cell, U_{ij}^{la} is a $s \times (2l+1) \times (2l+1)$ component vector. Therefore, $\tilde{D}$, $\tilde{\Gamma}_{UU}$, and $\tilde{\Phi}_{UU}$ are square matrices of dimensions $s \times (2l+1)^2$. Similarly, as for a given sublattice L_{ρ} has three components ($p = \pm 0$), the square matrices $\tilde{B}$, $\tilde{\Gamma}_{LL}$, and $\tilde{\Phi}_{LL}$ are of dimensions $3s$. Consequently $\tilde{C}$ is a rectangular matrix with $s \times (2l+1)^2$ rows and $3s$ columns, where we have assumed that all s molecules per unit cell are ordered. If only $n < s$ molecules are ordered (phase with partial disorder), all elements of $\tilde{C}$ that refer to the $s - n$ disordered molecules vanish.

V. DISCUSSION

Equations (4.9a) and (4.9b) describe the relaxation of orientational correlations and angular momentum, respectively. Both sets of equations are coupled through the restoring forces. We will discuss this system for several cases: fully ordered and fully disordered phases and phases of partial order.

A. Fully ordered phases

We assume that all s molecules per unit cell are ordered. By elimination of $\tilde{\Phi}_{LU}$, the system (4.9a) and (4.9b) reduces to a single set of equations for $\tilde{\Phi}_{UU}$:

$$[(\tilde{1}\omega + i\tilde{\Gamma}_{UU}) - \tilde{C}^{\tau}\tilde{B}(\tilde{1}\omega + i\tilde{\Gamma}_{LL})^{-1}\tilde{C}\tilde{D}]\tilde{\Phi}_{UU}(\omega) = \tilde{D}^{-1} \ . \quad (5.1)$$

We will discuss this equation first for the case of negligible damping. Neglecting $\tilde{\Gamma}_{UU}$ and $\tilde{\Gamma}_{LL}$, we obtain from Eq. (5.1)

$$[\tilde{1}\omega^2 - \tilde{C}^{\tau}\tilde{B}\tilde{C}\tilde{D}]\tilde{\Phi}_{UU}(\omega) = \omega D^{-1} \ . \quad (5.2)$$

The quantity $\tilde{C}^{\tau}\tilde{B}\tilde{C}\tilde{D} \equiv \tilde{M}$ plays the role of the dynamical matrix. Let us denote by $\mathbf{e}^{\alpha}$ and $(\omega^{\alpha})^2$ the orthonormalized eigenvectors and eigenvalues of the matrix $\tilde{M}$, respectively, such that

$$M_{\rho\sigma} = \sum_{\alpha} e_{\rho}^{\alpha}(\omega^{\alpha})^2 e_{\sigma}^{\alpha *} \quad (5.3a)$$

and

$$\sum_{\alpha} e_{\rho}^{\alpha} e_{\sigma}^{\alpha *} = \delta_{\rho\sigma}, \qquad \sum_{\rho} e_{\rho}^{\beta} e_{\rho}^{\alpha *} = \delta_{\alpha\beta} \ . \quad (5.3b)$$

Here α and β are eigenvalue indices while ρ and σ denote the indices of the U functions including the sublattice index. We have not written explicitly the $\mathbf{q}$ dependence of eigenvalues and eigenvectors. The number of eigenvalues is determined by the rank of the matrix $\tilde{M}$. The smallest matrix in the product $\tilde{C}^{\tau}\tilde{B}\tilde{C}\tilde{D}$ is given by $\tilde{B}$ that is of dimension $3s \times 3s$. Consequently, the rank of the matrix M is $\max(3s)$, s being the number of molecules per unit cell. This determines the number of eigenmodes $(\omega^{\alpha})^2$, that is $\leq 3s$. The same number $3s$ is obtained in usual libron dynamics.[8] With the help of relations (5.3a) and (5.3b), Eq. (5.2) can be rewritten as

$$\Phi_{U\gamma U\tau} = \omega \sum_{\beta\rho} \frac{e_{\gamma}^{\beta} e_{\rho}^{\beta *} D_{\rho\tau}^{-1}}{\omega^2 - (\omega^{\beta})^2} \ . \quad (5.4)$$

From the previous considerations it is obvious that the eigenfrequencies ω^{β} are proportional to the order parameter $\langle\sigma\rangle$ times the square root of the inverse susceptibility $\tilde{D} = (U, U)^{-1}$. This behavior is well known in magnetic systems[27] and in hydrodynamic phonon systems.[29] It is an advantage of the present treatment over the anharmonic libron theory[10] that this result, which is crucial for the temperature dependence of the libron resonances near T_c, is obtained in a straightforward way. It follows directly from the most appropriate choice of dynamic variables, i.e., U and L. Near T_c where the amplitudes of rotational oscillations are of course very large, the choice of Euler angles and their conjugate momenta as dynamic variables is very inadequate. Renormalized harmonic theories[4,5,8] that are based on a series expansion of the rotational potential in terms of Euler angles and a subsequent resummation of all even order anharmonicities are not appropriate to treat the transition from the fully ordered to the disordered region. In addition to an incomplete treatment of the renormalization of the real resonances (librons), the neglect of uneven order anharmonicities leads also to the complete absence of damping. The present theory suffers not from such deficiencies.

B. Disordered phases

With increasing temperature such that T reaches the transition temperature T_c, Eq. (5.2) is of course inadequate and we have to return to Eq. (5.1). For $T \to T_c$, $\tilde{C} \to 0$ as $\langle\sigma\rangle \to 0$ and becomes negligible. Then Eq. (5.1) reduces to

$$[(\tilde{1}\omega + i\tilde{\Gamma}_{UU})]\tilde{\Phi}_{UU}(\omega) = \tilde{D}^{-1} \ . \quad (5.5)$$

This equation describes the critical dynamics and the dynamics in the disordered phase. It has been used in Ref. 11 to explain the neutron scattering results on critical dynamics in CD_4H. One of the essential points of Ref. 11 is that the full matrix character of Eq. (5.5) has to be taken into account in order to describe the temperature dependence of the width of the central resonance in the dynamic scattering law.[12] We will not pursue this point further here.

In addition to Eq. (5.5), we find from Eq. (4.9b)

$$\tilde{\Phi}_{LU}(\omega) = (\omega\tilde{1} + i\tilde{\Gamma}_{LL})^{-1} i\tilde{C}\tilde{D}\tilde{\Phi}_{UU} \ . \quad (5.6)$$

This expression shows that with $\tilde{\Phi}_{UU} \neq 0$, the angular momentum relaxation becomes irrelevant for $(\tilde{C}/\tilde{\Gamma}_{LL}) \to 0$, as is the case for $T \to T_c$ or for disordered molecules in phases of partial order. Therefore Eq. (5.5) is the only relevant expression for the disordered phase and the critical region.

C. Partially ordered phases

The system of equations (4.9a) and (4.9b) is also appropriate to discuss partially ordered phases where $n < s$ molecules per unit cell are orientationally ordered while $s - n$ remain disordered.[25] Making an explicit distinction between ordered and disordered molecules by indices o and d, respectively, we rewrite (4.8) in 4×4 block-matrix form. Here we make use of the fact that the restoring forces $\tilde{C}$ vanish for disordered molecules. Then we obtain instead of Eqs. (4.9a) and (4.9b) the coupled set

$$(\tilde{1}\omega + i\tilde{\Gamma}_{UU}^{oo})\tilde{\Phi}_{UU}^{oo} + i\tilde{\Gamma}_{UU}^{od}\tilde{\Phi}_{UU}^{do} + i\tilde{C}\tilde{B}^{oo}\tilde{\Phi}_{LU}^{oo} = \tilde{D}^{oo-1} \ , \quad (5.7a)$$

$$i\tilde{\Gamma}_{UU}^{do}\tilde{\Phi}_{UU}^{oo} + (\tilde{1}\omega + i\tilde{\Gamma}_{UU}^{dd})\tilde{\Phi}_{UU}^{do} = \tilde{D}^{do-1} \ , \quad (5.7b)$$

$$-i\tilde{C}^{\tau}\tilde{D}^{oo}\tilde{\Phi}_{UU}^{oo} + (\tilde{1}\omega + i\tilde{\Gamma}_{LL}^{oo})\tilde{\Phi}_{LU}^{oo} + i\tilde{\Gamma}_{LL}^{od}\tilde{\Phi}_{LU}^{do} = \tilde{0} \ , \quad (5.7c)$$

$$i\tilde{\Gamma}_{LL}^{do}\tilde{\Phi}_{LU}^{oo} + (\tilde{1}\omega + i\tilde{\Gamma}_{LL}^{dd})\tilde{\Phi}_{LU}^{do} = \tilde{0} \ . \quad (5.7d)$$

In principle it is not difficult to eliminate $\tilde{\Phi}_{LU}^{oo}$, $\tilde{\Phi}_{LU}^{do}$, and $\tilde{\Phi}_{UU}^{do}$, thereby obtaining a closed equation for $\tilde{\Phi}_{UU}^{oo}$. However, we can obtain a more tractable expression for $\tilde{\Phi}_{UU}^{oo}$ by observing that the angular momentum relaxation of the disordered molecule is sufficiently fast, such that Eq. (5.7d) leads to

$$\tilde{\Phi}_{LU}^{do}(\omega) = -i(\tilde{1}\omega + i\tilde{\Gamma}_{LL}^{dd})^{-1}\tilde{\Gamma}_{LL}^{do}\tilde{\Phi}_{LU}^{oo} \to 0 \ . \quad (5.8)$$

This permits us to assume that $\tilde{\Phi}^{do}_{LU}$ is negligible in the set (5.7a)–(5.7d). Equivalently, we assume that the angular momentum of the disordered molecule does not fall within the set of secular variables. Then we obtain as a closed equation for $\tilde{\Phi}^{oo}_{UU}(\omega)$

$$[(\tilde{1}\omega + i\tilde{\Gamma}^{oo}_{UU}) - \tilde{C}^{\tau}\tilde{B}(\tilde{1}\omega + i\tilde{\Gamma}^{oo}_{LL})^{-1}\tilde{C}\tilde{D}^{oo} + \tilde{\Xi}^{od}(\omega)\tilde{\Gamma}^{do}_{UU}]\tilde{\Phi}^{oo}_{UU}(\omega)$$
$$= \tilde{D}^{oo^{-1}} - i\tilde{\Xi}^{od}(\omega)D^{do^{-1}} , \tag{5.9a}$$

where we have defined

$$\tilde{\Xi}^{od}(\omega) = \tilde{\Gamma}^{od}_{UU}(\tilde{1}\omega + i\tilde{\Gamma}^{dd}_{UU})^{-1} . \tag{5.9b}$$

Comparing Eq. (5.9a) with Eq. (5.1), we see as an essential difference that through the function Ξ, the orientational relaxation of the disordered molecules is included. As we will see, this relaxation of the disordered molecules leads to an additional resonance in the dynamic scattering law. In a previous paper,[10] this relaxation was already included. However, the description of the ordered molecules was formulated in terms of Euler angles φ and conjugate momenta π and was thus inferior to the present approach.

Finally, we want to mention that from the system (4.9a) and (4.9b) one can easily derive a closed equation for the relaxation function of the disordered molecules $\tilde{\Phi}^{dd}(\omega)$.

VI. DYNAMIC SCATTERING LAW

In the previous section, we derived and discussed the basic expressions for the orientational relaxation function. Now we will consider in more detail the resonances of the dynamic scattering law. We have in mind here primarily neutron and light scattering experiments.

As has been shown previously,[10] the dynamic scattering law can be written as

$$S(\mathbf{Q}, \omega) = \sum_{\substack{\mu,\nu \\ a,b}} F^{ab}_{\mu\nu}(\mathbf{Q}) S^{ab}_{\mu\nu}(\mathbf{q}, \omega)\Delta(\mathbf{Q} - \mathbf{q}) , \tag{6.1}$$

where

$$S^{ab}_{\mu\nu}(\mathbf{q}, \omega) = \frac{1}{2\pi}\int \langle U^a_{\mu}(\mathbf{q}, t)U^b_{\nu}(-\mathbf{q}, 0)\rangle e^{i\omega t}\, dt \tag{6.2}$$

is the dynamic orientational correlation functions and where F is a form factor that follows essentially from an expression of the scattering length in terms of symmetry adapted functions.[15] The indices μ and ν collectively denote the indices (l, i, j) of the U function, while a and b are sublattice indices (see Sec. III). The quantity $\Delta(\mathbf{k})$ is a pseudo-delta-function given by $\sum_{\tau}\delta_{\tau,\mathbf{k}}$, where τ is a vector of the reciprocal lattice. From Eqs. (2.4b) and (2.5) we immediately find the connection between the scattering law and Kubo's relaxation function:

$$S^{\alpha\beta}(q, \omega) = -[1 - \exp(-\omega/T)]^{-1}\omega\, \mathrm{Im}\Phi^{\alpha\beta}_{UU}(q, \omega) . \tag{6.3}$$

Here α, β stand for the indices (a, μ) and (b, ν). The procedure to follow is now straightforward. From Eqs. (5.1) or (5.9a) one obtains Φ, and from there, by taking the imaginary part, S.

Restricting ourselves to a single ordered mode, we neglect the matrix character of Eqs. (5.9). This is equivalent to the consideration of one ordered and one disordered sublattice. With the definitions

$$D^{oo^{-1}} = d , \quad \bar{\omega}^2 = CBCD^{oo} , \quad \Gamma^{oo}_{UU} = \lambda , \quad \Gamma^{oo}_{LL} = \eta ,$$
$$\Gamma^{od}_{UU} = \Gamma^{do}_{UU} = \xi , \quad \Gamma^{dd}_{UU} = \zeta , \quad D^{od^{-1}} = b , \tag{6.4}$$

we rewrite Eq. (5.9a)

$$\left((\omega + i\lambda) - \frac{\bar{\omega}^2}{\omega + i\eta} + \frac{\xi^2}{\omega + i\zeta}\right)\Phi^{oo}_{UU}(\omega) = d - \frac{i\xi b}{\omega + i\zeta} , \tag{6.5}$$

and therefore we readily obtain

$$\mathrm{Im}\Phi^{oo}_{UU}(\omega) = \frac{X_1 Y_2 - X_2 Y_1}{X_1^2 + X_2^2} \tag{6.6a}$$

with

$$X_1 = \omega^2 - \bar{\omega}^2 - \lambda\eta + \xi^2\frac{(\omega^2 + \eta\zeta)}{\omega^2 + \zeta^2} , \tag{6.6b}$$

$$X_2 = \omega\left[\lambda + \eta + \xi^2\left(\frac{\eta - \zeta}{\omega^2 + \zeta^2}\right)\right] , \tag{6.6c}$$

$$Y_1 = \omega\left[d + \xi b\left(\frac{\eta - \zeta}{\omega^2 + \zeta^2}\right)\right] , \tag{6.6d}$$

$$Y_2 = \eta d - \xi b\left(\frac{\omega^2 + \eta\zeta}{\omega^2 + \zeta^2}\right) . \tag{6.6e}$$

We see that for $\xi = 0$, the coupling to the disordered sublattice disappears. If in addition we take $\bar{\omega} \neq 0$, Eq. (6.5) describes the dynamics of the fully ordered phase (Sec. V.A with inclusion of the damping terms η and λ). For $\bar{\omega} = 0$, Eq. (6.5) corresponds to the fully disordered phase (Sec. V.B). In other words, depending on the values of the parameters ξ and $\bar{\omega}$, Eq. (6.5) gives a complete description of the dynamics of ordered phases, disordered phases, and partially ordered phases.

We have plotted $-\Phi''(\omega) = -\mathrm{Im}\Phi(\omega)$, taken from Eq. (6.6a), as a function of ω for several temperatures (Fig. 1). We have thereby used molecular field expressions[24] for C, D^{oo} as functions of T while B has been taken constant. Having in mind a comparison with neutron experiments[12] in CD_4H, we have chosen the initial values at $T = 22\,^{\circ}\mathrm{K}$ as follows: $\bar{\omega} = 5$ meV is taken from Ref. 8; for the order parameter $\langle\sigma\rangle$, we take $\frac{3}{4}$ (Ref. 14); while $\eta = 2$ meV and $\lambda = 1.6$ meV. The value of η is cho-

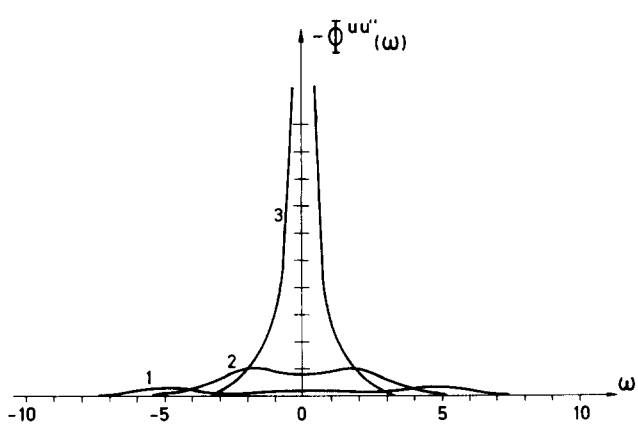

FIG. 1. Plot of $-\mathrm{Im}\Phi^{UU}$ as function of ω (in meV) and the temperature for $\lambda = 1.6$ meV, $\eta = 2$ meV, $\xi = 0.2$ meV, $\zeta = 0$ meV. (1) $T = 22\,^{\circ}\mathrm{K}$, (2) $T = 24\,^{\circ}\mathrm{K}$, (3) $T = 26\,^{\circ}\mathrm{K}$.

sen such that for $\lambda = 0$, one gets well defined librons. The value 1.6 meV for λ follows from an extrapolation of the experimental results[12] by using molecular field theory for the temperature dependence of D^{oo}. The influence of the central (disordered) molecules has been accounted for by taking $\zeta = 0.04|T - T_c|$ and several values (0.02 and 0.0 meV) for ξ. We have hereby taken into account the stability condition $(\lambda\zeta - \xi^2) > 0$ for the dissipative coefficients.

From the numerical results it follows that the influence of the central molecule on the libron spectrum is very small; in particular, the influence of the libron damping is quasinegligible. Therefore we conclude that the central molecule is not responsible for the overdamping of librons in CD_4II.[12] On the other hand, our calculations show that the transport coefficient λ is, in addition to η, the essential quantity that is responsible for the overdamping of librons.

VII. CONCLUSIONS

The aim of our work has been to present the rotational dynamics of molecular crystals from a unified point of view. This means that we made a theory that is able to treat the following cases within the same framework:

(a) *Orientationally ordered phases* ($T < T_c$) where the molecules carry out rotational oscillations around well defined equilibrium positions, the amplitudes of these oscillations can be large (very anharmonic regime);

(b) The region of *critical dynamics* ($T \simeq T_c$);

(c) *The disordered region* ($T > T_c$) or plastic phase where the molecules have no preferential orientations and carry out a motion of hindered rotational diffusion;

(d) *Phases of partial order* where at the same time the molecules on some definite lattice points are orientationally ordered [as are all molecules in Case (a)], while the molecules on some definite other lattice point are orientationally disordered [like Case (c) for all molecules].

The set of basic matrix equations (4.8) enables us to describe the dynamics of all these cases continuously as a function of temperature.

This is the main advantage of the present treatment in comparison with previous work,[10,11] where one had to use separate descriptions for these cases. The simplicity of the present theory is mainly due to the correct choice of secular variables, namely, the symmetry adapted functions U and the angular momentum operators L. Then the full power of the projection operator technique[17] can be exploited to derive the dynamic equations. As our main result we then obtain two coupled sets of matrix equations (4.8) for the dynamics of the orientation correlations and the angular momenta, respectively. Both equations are coupled through the restoring forces that are found to be proportional to the order parameter $\langle U^l \rangle \neq 0$. In addition, the relaxation of orientational correlations and of angular momentum correlations are described by transport coefficients Γ_{UU} and Γ_{LL}, respectively. The transport coefficient Γ_{UU} has no direct analog in ordinary lattice dynamics. By approaching T_c, both sets of equations decouple as $\langle U^l \rangle \to 0$, and we are left with a pure relaxation equation that describes the critical dynamics, as was discussed previously.[11] If we take $\langle U \rangle = 0$ at some lattice points in the ordered phase, we are able to discuss phases of partial order. A practical relevant example is CD_4II.[6]

Some attention is devoted to a discussion of libron damping in the ordered phase. We conclude from our analysis that the critical quantity for the (over)damping of librons in CD_4II[12] is the transport coefficient Γ_{UU}. This transport coefficient is important in the ordered phase wherever the amplitude of the orientational oscillations are sufficiently large such that a purely harmonic theory or even a renormalized harmonic theory breaks down. On the other hand, our calculations seem to indicate that the influence of the central (disordered) molecules on libron damping is rather small.

We have neglected here the energy in the set of secular variables. This problem has been treated previously[10,11] and brings no further insight in the present work.

A more serious approximation is the neglect of translational degrees of freedom. It is well known that in some molecular crystals,[30,31] the interaction between translational and rotational degrees of freedom is important. Our answer to this objection is that we restrict ourselves here deliberately to rotational degrees of freedom. One has to understand both the dynamics of rotational and translational degrees of freedom separately before one is able to treat their coupling. At present we are working on this problem.

Finally we should mention that the present treatment of the dynamics of phases of partial order is also relevant in order to explain the proton spin conversion in CH_4.[32,33,25] We are at present working out the theory to explain these experiments.

ACKNOWLEDGMENTS

The authors thank D. Kroll, A. Hüller, F. Schwabl, and J. Naudts for useful discussions.

APPENDIX A

The U functions are related to the D functions by[24]

$$U^l_{mn} = \sum_{m'n'} S^{l*}_{m'm} S^l_{n'n} D^l_{m'n'} , \tag{A1}$$

$$D^l_{m'p} = \sum_{rs} S^l_{rm'} S^{l*}_{sp} U^l_{rs} . \tag{A2}$$

Here and in the following all lower subscripts run from $-l$ to l; S is a unitary matrix; and S^* is its complex conjugate. Using Eqs. (3.7) and (A2) and the orthogonality of S we find

$$L_q U^l_{mn} = \sum_{m'n'} \sum_{p} S^{l*}_{m'm} S^l_{n'm} a^{ql}_{n'p} D^l_{m'p} \qquad q = 0, \pm \tag{A3}$$

$$= \sum_{m'n'} \sum_{p} \sum_{rs} S^{l*}_{m'm} S^l_{n'n} a^{ql}_{n'p} S^l_{rm'} S^l_{sp} U^l_{rs} \tag{A4}$$

$$= \sum_{n'p} \sum_{s} S^l_{n'n} a^{ql}_{n'p} S^{l*}_{sp} U^l_{ms} \tag{A5}$$

$$= \sum_s c_{ns}^{ql} U_{ms}^{l} \,. \tag{A6}$$

In order to show that the coefficients b_{jk}^{pl} are real we have to prove that $c_{ns}^{ql} + c_{ns}^{ql*} = 0$. Using the notation of James and Keenan,[24] Eq. (3.8) and the relation $S_{sp}^{l} = (-1)^s S_{-sp}^{l*}$, $s = -(2l+1) \cdots (2l+1)$ we find for $q = 0$:

$$C_{ns}^{0l*} = \sum_p p S_{pn}^{l*} S_{sp}^{l} \tag{A7}$$

$$= \sum_p p S_{-pn}^{l} S_{s-p}^{l*} \tag{A8}$$

$$= -\sum_p p S_{pn}^{l} S_{sp}^{l*} \tag{A9}$$

$$= -C_{ns}^{0l} \,. \tag{A10}$$

For $q = +$ we have

$$C_{ns}^{+l*} = (C_{sn}^{+l})^{\dagger} = \sum_p \sqrt{(l+p+1)(l-p)/2}\; S_{sp+1}^{l*} S_{pn}^{l} \tag{A11}$$

$$= -\sum_p \sqrt{(l+p+1)(l-p)/2}\; S_{s-p-1}^{l} S_{-pn}^{l*} \tag{A12}$$

$$= -\sum_p \sqrt{(l-p+1)(l+p)/2}\; S_{sp-1}^{l} S_{pn}^{l*} \tag{A13}$$

$$= -\sum_p \sqrt{(l-p)(l+p+1)/2}\; S_{sp}^{l} S_{p+1n}^{l*} \tag{A14}$$

$$= -C_{ns}^{+l} \,.$$

In the same way we obtain $C_{ns}^{-l} = -C_{ns}^{-l}$. Therefore we may conclude that we can write Eq. (A6) as

$$L_q U_{mn}^{l} = i \sum_s b_{ns}^{ql} U_{ms}^{l}, \qquad b_{ns}^{ql} \text{ real.} \tag{A15}$$

*Supported by the Project "Neutron Scattering," I. I. K. W., Belgium.

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